U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-281 492

Industrial Process Profiles for Environmental Use: Chapter 26 Titanium Industry

Radian Corp. Austin, Tex

Prepared for

Industrial Environmental Research Lab -Cincinnati, Ohio

Feb 77

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/2-77-023z	2.	3. RECIPIENT'S ACCESSION NO. PB261492
4. TITLE AND SUBTITLE Industrial Process Profiles for Environmental Use: Chapter 26. Titanium Industry		5. REPORT DATE February 1977 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Vishnu S. Katari & Timothy W. Devitt (PEDCo) Terry B. Parsons, Editor		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Radian Corporation 8500 Shoal Creek Boulevard P.O. Box 9948 Austin, Texas 78766		10. PROGRAM ELEMENT NO. 1AB015: ROAP 21AFH-025 11. CONTRACT/GRANT NO. 68-02-1319, Task 34
12. SPONSORING AGENCY NAME AND ADDRESS Industrial Environmental Research Laboratory Office of Research and Development U.S. ENVIRONMENTAL PROTECTION AGENCY Cincinnati, Ohio 45268		13. TYPE OF REPORT AND PERIOD COVERED Initial: 8/75-11/76 14. SPONSORING AGENCY CODE EPA/600/12

15. SUPPLEMENTARY NOTES

16. ABSTRACT

The catalog of Industrial Process Profiles for Environmental Use was developed as an aid in defining the environmental impacts of industrial activity in the United States. Entries for each industry are in consistent format and form separate chapters of the study.

The titanium industry produces two principal products, titanium metal and titanium dioxide. For purposes of analyses, therefore, the industry is considered in two segments: titanium metal production and titanium dioxide production. Two industrial process flow diagrams and eleven process descriptions have been prepared to characterize the industry. Within each process description available data have been presented on input materials, operation parameters, utility requirements, and waste stream. Data related to the subject matter, including composition and properties of titanium products, as well as producer listings, are included as appendices.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution Titanium Industry Titanium Metal Titanium Dioxide Pigment Process Description	Air Pollution Control Water Pollution Control Solid Waste Control Stationary Sources Titanium Industry	07B 11C 13B

18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS (This Report) Unclassified 20. SECURITY CLASS (This page) Unclassified	21. NO. OF PAGES 67 22. PRICE PCA04 MFA01

EPA Form 2220-1 (9-73)

*USGPO: 1978 — 757-086/0807

PB 281 492

EPA-600/2-77-023z
February 1977

Environmental Protection Technology Series

INDUSTRIAL PROCESS PROFILES FOR ENVIRONMENTAL USE: Chapter 26. Titanium Industry

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

Industrial Environmental Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into five series. These five broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The five series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies

This report has been assigned to the ENVIRONMENTAL PROTECTION TECHNOLOGY series. This series describes research performed to develop and demonstrate instrumentation, equipment, and methodology to repair or prevent environmental degradation from point and non-point sources of pollution. This work provides the new or improved technology required for the control and treatment of pollution sources to meet environmental quality standards.

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

EPA-600/2-77-023z
February 1977

INDUSTRIAL PROCESS PROFILES

FOR ENVIRONMENTAL USE

CHAPTER 26

TITANIUM INDUSTRY

by

Vishnu S. Katari and Timothy W. Devitt
PEDCo-Environmental Specialists, Inc.
Cincinnati, Ohio 45226

Contract No. 68-02-1321

Project Officer
I. A. Jefcoat
Industrial Environmental Research Laboratory
Research Triangle Park, North Carolina 27711

INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

DISCLAIMER

This report has been reviewed by the Industrial Environmental Research Laboratory - Cincinnati, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

TABLE OF CONTENTS

CHAPTER 26

	Page
INDUSTRY DESCRIPTION	1
Raw Materials	4
Products	5
Companies	6
Environmental Impact	7
INDUSTRY ANALYSIS	9
Titanium Metal Production	10
Process No. 1. Mining	12
Process No. 2. Ore Upgrading	16
Process No. 3. Smelting	23
Process No. 4. Chlorination and Purification	24
Process No. 5. Reduction	26
Process No. 6. Melting and Ingot Conditioning	29
Process No. 7. Fabrication	31
Titanium Dioxide Production	33
Process No. 8. Oxidation	35
Process No. 9. Digestion, Crystallization, Hydrolysis, and Bleaching	36
Process No. 10. Calcination	38
Process No. 11. Finishing Operations	40
APPENDIX A - Composition and Properties of Titanium Products	41
APPENDIX B - Titanium and Titanium Oxide Producers	51
APPENDIX C - References for Appendices	55

LIST OF FIGURES

CHAPTER 26

Figure		Page
1	Titanium Metal Production.	11
2	Titanium Dioxide Production.	34

LIST OF TABLES

CHAPTER 26

Table		Page
1	Salient Titanium Statistics, 1973.	2
2	U.S. Production and Consumption of Titanium, 1974. . . .	3
3	Distribution of Titanium Mill Products in 1974	6
4	Chemical Composition of Raw Waste Water from Titanium Open-Pit Mine.	14
5	Reagent Use in Flotation Circuit of Mill at Open-Pit Mine.	17
6	Chemical Composition of Raw Waste Water at Two Dredge Mills	18
7	Chemical Compositions of Raw Waste Water and Treated Recycle Water from the Mill at Open-Pit Mine	20
8	Material Balance for Melting Operations at Titanium Plants.	29
9	Materials Balance for Fabrication of Mill Products . . .	31
10	Materials Required for Producing One Ton of Titanium Dioxide	37
11	Analysis of Effluent Gases of a TiO_2 Calciner	39
A-1	Analysis of Ilmenite Ore (Percent)	42

Table		Page
A-2	Range of Composition of Titanium Concentrates	43
A-3	Chemical Analysis of Titanium Metal	44
A-4	Physical Properties of Commercially Pure Titanium	45
A-5	Physical Properties of Titanium Dioxide	46
A-6	Typical Titanium Sponge Analysis	47
A-7	Chemical Analyses of Commercial Grade and Purified $TiCl_4$ from Sources A and B	48
A-8	Physical Properties of Titanium Tetrachloride	49
A-9	Typical Properties of Commercial Titanium Alloys	50
B-1	Titanium Industry Companies, 1972	52

ACKNOWLEDGEMENTS

This chapter of the Environmental Catalog of Industrial processes was prepared by PEDCo-Environmental Specialists, Inc. The contributions of Vishnu S. Katari and Timothy W. Devitt are gratefully acknowledged.

TITANIUM INDUSTRY

INDUSTRY DESCRIPTION

The titanium industry produces two principal products, titanium metal and titanium dioxide. For purposes of analysis, therefore, the industry is considered in two segments: titanium metal production and titanium dioxide production.

In 1968, approximately 700 workers were employed in the United States in mining and concentrating titanium minerals, including by-product and coproduct materials such as zircon and monazite; about 10,000 workers were employed in titanium pigment production and an estimated 2,500 workers were employed in producing titanium sponge metal, ingot and mill products.[1] In 1974, an estimated 800 people were employed in ilmenite mining and milling, and 10 people were employed in rutile mining and milling. Titanium metal reduction plants employed about 950 people.[2]

Table 1 presents ore production and consumption data for the United States in 1973.[3] In 1974, the domestic ingot production capacity was approximately 36 million kilograms and the actual production reached slightly more than 33 million kilograms. Aerospace applications, including both military and commercial aircraft, accounted for the bulk of U.S. demand for titanium metal. Consumption in other applications, particularly chemical processing equipment, power generation, and petrochemicals continued to grow at an accelerated rate. In 1974, the titanium pigment production was 715,000 tons. Table 2 presents the U.S. production and consumption data for titanium in 1974.[4]

Domestic demand for titanium for the year 2000 is expected to be between 100 to 350 million kilograms. This demand is mainly attributed to the use of titanium for applications in the aerospace and chemical

Table 1. SALIENT TITANIUM STATISTICS, 1973

Material	Quantity, tons[a]
Ilmenite Concentrate:	
Mine shipments	737,900
Imports	63,222
Titanium Slag:	
Imports	215,227
Consumption	255,635
Rutile Concentrate:	
Imports	189,427
Consumption	251,205

[a] Metric ton (1000 kg).

Table 2. U.S. PRODUCTION AND CONSUMPTION OF TITANIUM, 1974

Material	Quantity, tons[a]
Sponge:	
Imports	6,305
Consumption	24,948
Scrap: Consumption	9,707
Ingot:	
Production	33,249
Consumption	28,486
Mill product shipments	15,649
Titanium Pigment:	
Production	715,000

[a] Metric ton (1000 kg).

industries and the manufacture of paints, varnishes and lacquers, papers, plastics and floor coverings.

Raw Materials

The most common titaniferous materials are anatase, ilmenite, leucoxene, and rutile. In addition, a few deposits contain large amounts of less common materials, such as Perovskite, Brookite, sphene, and magnetite, which also contain titanium.

Anatase is brown, crystallizes in the tetragonal system, and in the natural state contains 98.4 to 99.8 percent TiO_2. Ilmenite is iron black and crystallizes in the hexagonal system. It contains approximately 50 percent titanium dioxide, 30 to 50 percent iron oxides, and trace amounts of silica, alumina, and other metals.

Leucoxene is a fine-grained type of rutile or anatase, or mixtures of these with amorphous material. This material usually contains more than 68 percent TiO_2 and occurs with other titanium-bearing materials.

Rutile occurs as reddish-brown to red crystals of tetragonal structure or in granular masses. It is essentially pure TiO_2, but some deposits contain large amounts of ferric iron, tantalum, or columbium. Virtually all of the rutile used in the United States is imported.

Titanium slag may also be considered an ore. It is produced by smelting a mixture of carbon and titanium-bearing material to yield molten iron and slag containing about 70 to 90 percent TiO_2. Analysis of domestic ilmenite ore, upgraded ore concentrate and Canadian slag are given in the Tables A-1 and A-2 in appendix A.

Additional raw materials generally are not required for beneficiation of titanium ores, although some coke is added to hematite, ilmenite and magnetic ilmenite ores in upgrading processes. Considerable quantities of chlorine are required to produce titanium tetrachloride, $TiCl_4$, an intermediate raw material for titanium metal and pigment production. This chlorine is later liberated when the $TiCl_4$ is converted to TiO_2. When titanium metal is produced, the chlorine is

converted to magnesium chloride or sodium chloride. Some plants recover the reductant metal and chlorine by electrolysis.

Products

Titanium is a low-density, silvery-white metal important for its high strength-to-weight ratio and its resistance to corrosion. It is 61 percent heavier than aluminum but only 56 percent as heavy as alloy steel. The strength-to-weight ratio below 540°C exceeds that of aluminum and of stainless steel. Table A-3 in appendix A gives a chemical analysis of titanium metal of commercial grades and Table A-4 gives the physical properties of pure titanium metal.

Titanium dioxide pigment is sold domestically in three grades. Rutile and anatase grades are fairly pure titanium dioxide, but because of differences in crystal structure they differ in their covering and chalking characteristics. Each is 95 to 99 percent pure TiO_2. Extended titanium pigment as sold commercially contains only 30 to 50 percent TiO_2. Table A-5 in appendix A lists the physical properties of titanium dioxide. Titanium sponge is an elemental metal product with a sponge-like appearance, obtained by reducing $TiCl_4$ with magnesium or sodium. Table A-6 presents a typical analysis of titanium sponge.

The chemical analysis of commercial-grade and purified titanium tetrachloride and physical properties of titanium tetrachloride are given in Tables A-7 and A-8 in appendix A. As mentioned earlier, titanium tetrachloride, $TiCl_4$, is an intermediate product used in the manufacture of both titanium metals and pigments. It is a volatile, colorless liquid.

Titanium ingots include three types, classified according to their predominant crystal structure: alpha, alpha-beta, and beta. Aluminum is the most prominent alpha-stabilizing addition. Alpha-beta alloys contain some aluminum, but also contain other metals to stabilize the beta phase. The beta alloys also have a mixed alpha-beta structure, but are predominantly beta. About 20 commercial and semicommercial titanium

alloys are available to the titanium user.[1] Table A-9 in appendix A gives typical properties of commercial titanium alloys.

Historically, the major fabricated product of the titanium metal industry has been billets, which formerly accounted for some 60 percent of all product shipments from titanium mills. The forging billet share of shipments decreased to 42 percent in 1974. Meanwhile the share of tubing and flat-rolled products (sheet, strip, and plate) increased. Table 3 presents data on the distribution of titanium mill products in 1974.[4]

Table 3. DISTRIBUTION OF TITANIUM MILL PRODUCTS IN 1974

Product	Quantity, kilograms
Sheet, strip, plate	4,977
Forging and extrusion billet	64,729
Rod and bar	2,167
Wire	790
Pipe, tubing extrusions	1,251

Companies

In 1971, 10 companies produced titanium dioxide (TiO_2) and five companies were involved in producing titanium concentrates in five different states. Titanium metal was produced by three corporations owned by six companies. Nine companies produced titanium ingots from sponge metal and scrap.

In 1973, rutile-type pigment accounted for 72 percent of total pigment production and was produced by seven manufacturers. Anatase-type pigment was produced by five companies.[3] Appendix Table B-1 lists the companies involved in the titanium industry, their locations and operations. During 1974, four mines located in New Jersey, Virginia, and Florida produced titanium ore in the United States.[5]

Environmental Impact

Large quantities of wastes are generated from the mining and concentrating of titanium and production of titanium dioxide. Disposal of these wastes, particularly those resulting from titanium dioxide production, represents a major environmental problem to the industry. Much of this waste consists of weak sulfuric acid which is disposed of by either deep sea dumping or neutralization. In 1972 domestic titanium dioxide plants produced about 1.7 million tons[a] of iron-acid sludge and 146 thousand tons of iron-chloride sludge.[6]

Air pollutants are also generated by the various processes. Major emission sources within the titanium industry are in the mining and beneficiation of ilmenite and production of TiO_2 pigment. Sulfur dioxide mist and particulate emissions occur from the calcination step in the sulfate process, and chloride emissions occur if calcination is performed in the chloride process.

[a] Metric tons (1000 kg) are used throughout this report.

BIBLIOGRAPHY

1. Stamper, J. W. Titanium. In: Mineral Facts and Problems, United States Department of Interior. Washington, D. C., U.S. Government Printing Office, 1970.

2. Personal communication with Mr. J. W. Stamper, Division of Minerals Studies. United States Department of Interior.

3. Wessel, F. W. Titanium. In: Bureau of Mines Minerals Yearbook, 1973 reprint. United States Department of Interior. Washington, D.C., U.S. Government Printing Office, 1975.

4. Minkler, W. W. Titanium - '74, A Boom Year; Demand Looks Good for '75. Engineering and Mining Journal. March 1975.

5. A Study of Waste Generation Treatment and Disposal in the Metals Mining Industry. Vol. I. MRI Report (Review Draft). EPA Contract No. 68-01-2665. May 1975.

6. Saxton, J. C., and M. Narkus-Kramer. EPA Findings on Solid Wastes From Industrial Chemicals. Chemical Engineering. April 28, 1975. 107 p.

INDUSTRY ANALYSIS

Information for this study was largely obtained from the literature. Emission data are very sparse and existing data are variable due to the variations in processing and raw materials. Also, most of the information regarding specific process operating conditions and utility requirements is not available.

The titanium industry is analyzed in two segments: production of titanium metal and production of titanium dioxide. Flow sheets are presented for each segment, and process descriptions are presented in the text.

Each process description outlines the function of the process, the input materials, energy requirements, and composition and rates of the waste streams.

TITANIUM METAL PRODUCTION

This industry segment includes those processes required to obtain and upgrade the ore and produce finished titanium metal as shown in Figure 1.

In the production of titanium metal, the ores are mined and upgraded by removal of impurities. The purified ilmenite ore (or imported rutile ore) is then chlorinated to form titanium tetrachloride. This chlorinated product is refined to high purity and reduced with magnesium or sodium at about 870° C to a spongy mass. Excess magnesium chloride or sodium chloride is removed by dilute acid leaching or vacuum distillation. The spongy mass of titanium is then broken into about 1 centimeter pieces for melting into ingots. The ingots are fabricated into various grades and shapes, and are subsequently used to produce alloys.

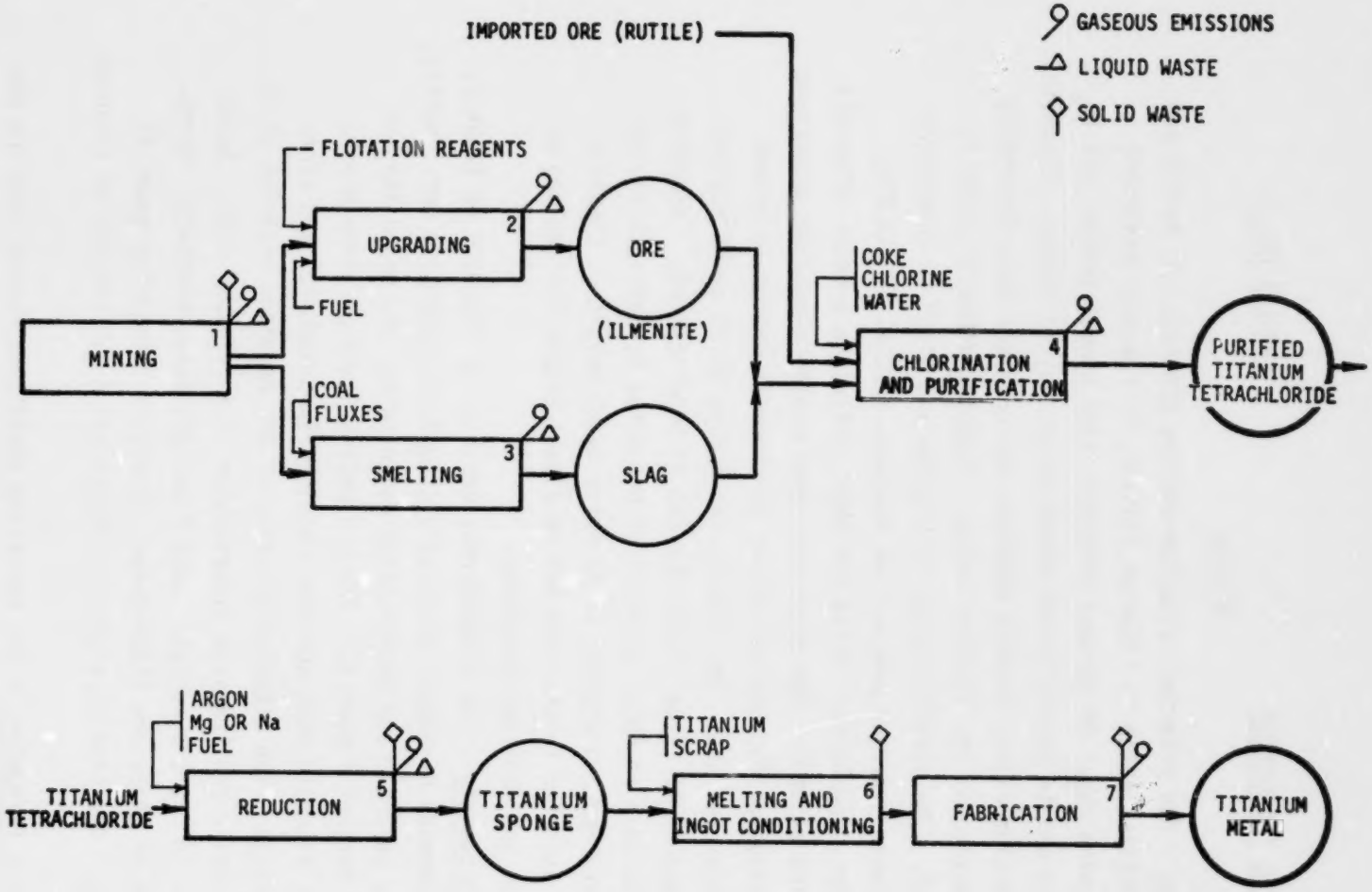

Figure 1. Titanium metal production.

TITANIUM METAL PRODUCTION PROCESS NO. 1

Mining

1. Function - The principal titanium-bearing minerals are rutile and ilmenite. Rutile, which is titanium dioxide, is the most desirable form, containing about 50 percent titanium after beneficiation, but it is less abundant and is generally not mined in the United States. Ilmenite, the iron titanium oxide, is more abundant but requires more processing before extraction of the titanium oxide. Ilmenite deposits occur in sand and rock. The ilmenite sands in Florida are mined by underwater suction dredges. Surface preparation includes removal of standing timber, stumps, and roots. Holes are then drilled at 6 meter intervals, and loaded and blasted. The sands are removed with a suction cutterhead capable of digging 1000 tons of solids per hour at depths 14 meters below the water surface. The slurry, consisting of 10 to 15 percent solids, is pumped to barges where the ore is beneficiated.[1] Ilmenite rock deposits such as those in New York are mined by open-pit mining. The ore is drilled and blasted in 10 meter bench heights. Electric shovels are used for loading the ore on diesel trucks for hauling to concentration and smelting processes.

2. Input Materials - The minable rock deposits of ilmenite at Tawahus, N.Y., are composed of masses of closely associated magnetite and ilmenite, separated by gabbroic and anorthositic waste zones. As mined the ore contains 32 percent ilmenite.[2] The ore bodies mined at Piney River, Va., contain ilmenite with apatite (calcium fluophosphate) and other gangue materials. The titanium deposits of the Roseland district of Va. consist of rutile and ilmenite disseminated in a feldspar rock. Sands being worked in Florida contain about 4 percent heavy minerals. Forty-five percent of these are titaniferous materials containing about 63 percent TiO_2. The sand as a whole contains about 1.8 percent of titanium mineral.[3]

3. Operating Parameters - The operating conditions depend upon the ore (sand or rock) deposit mined. Mining is carried out at ambient conditions.

4. Utilities - Energy in the form of electricity and diesel fuel is required for operation of the power mining equipment such as tractor and cutterhead.

5. Waste Streams - In the wet-mining of sand deposits, atmospheric emissions are minimal. The large-scale dredging operations must be kept isolated from other water bodies, however, to minimize potential water pollution.

Atmospheric emissions from rock mining operations are probably similar to those from other strip-mining activities. Approximately 1.2 tons of waste must be removed to obtain 1 ton of ore.[1] Both the blasting and the handling operations at the mine may release significant quantities of fugitive dust. One source reports the emission factor for titanium open-pit mining as 0.1 kg/ton, but indicates that the reliability of this factor is poor.[4] Hard rock mining of ilmenite is estimated to produce particles of 5 micrometers average diameter, ranging from 0.5 to 10 micrometers. Provisions should also be made for backfill and landscaping of the mine site after the ore is extracted. Without such treatment, erosion may lead to surface runoff, with associated water pollution problems. Only one open-pit mine is now operating. Table 4 gives the chemical composition of waste discharge from the mine.[5]

6. EPA Source Classification Code - None exists

Table 4. CHEMICAL COMPOSITION OF RAW WASTE WATER FROM TITANIUM OPEN-PIT MINE

Parameter	Concentration, mg/ℓ	Parameter	Concentration, mg/ℓ
Conductivity	1,000[a]	Pb	<0.05
Color	11.3[b]	Mg	26.0
Turbidity (JTU)	0.37	Total Mn	<0.01
TDS	1,240	Ni	<0.01
TSS	14	Tl	<0.1
Acidity	6.4	V	<0.5
Alkalinity	138.2	K	13.0
Hardness	546.4	Sr	0.129
COD	6.4	Ag	<0.01
TOC	10.3	Ns	140.0
Oil and grease	3.0	Se	0.75
MBAS surfactants	0.32	Te	<0.06
Total Kjeldahl N	2.24	Ti	<0.2
Al	0.1	Zn	0.007
As	0.1	Mo	<0.1
Be	0.003	Co	<0.1
Ba	<1	Phenol	<0.01
B	0.01	Chloride	183.5
Cd	<0.002	Fluoride	3.20
Ca	94.5	Sulfate	270
Cr	<0.01	Nitrate	15.52
Cu	<0.03	Phosphate	<0.05
Total Fe	0.33		

[a] Value in micromhos/cm.

[b] Value in cobalt units.

7. References:

1. Miller, A. Titanium, A Materials Survey. Bureau of Mines. Information Circular 7791. United States Department of Interior, Washington, D.C., U.S. Government Printing Office, September 1957.

2. Barksdale, Jelks. Titanium, Its Occurrence, Chemistry and Technology. New York, The Ronald Press Company, 1966.

3. Carpenter, J.H., et al. Mining and Concentration of Ilmenite and Associated Minerals at Trail Ridge, Fla. Mining Engineering. August 1953.

4. GCA Corporation. National Emissions Inventory of Sources and Emissions of Titanium. EPA Publication No. 450/3-74-008. Distributed by National Technical Information Service. May 1973.

5. Calspan Corporation. Draft Copy. Developement Document for Effluent Limitations Guidelines and Standards of Performance for the Ore Mining and Dressing Industry Point Source Category. EPA Contract No. 68-01-2682. April 1975.

TITANIUM METAL PRODUCTION PROCESS NO. 2

Ore Upgrading

1. Function - The dredged ilmenite sands are screened to remove material larger than 1/4-inch mesh and the slurry is dewatered to about 30 percent solids. The slurry is then passed through a concentration plant, usually mounted on a barge. Concentrates are pumped ashore at a concentration of 25 percent solids at a rate of 30 to 45 tons per hour. The material is dewatered and stockpiled for dry mill operations, where the concentrates are dried at 110°C and cleaned by a series of electrostatic and magnetic separators. Ilmenite remains in the magnetic fraction.[1]

Ores from rock deposits are crushed and ground in several stages by jaw crushers, cone crushers, and rod mills to produce a minus-28 mesh material. Wet magnetic separators remove the magnetic fraction of the material. The nonmagnetic fraction containing gangue and ilmenite is then concentrated on reciprocating tables or in flotation circuits, filtered, and dried.[2]

2. Input material - Commercially workable rock deposits contain approximately 17 to 35 percent TiO_2, principally as ilmenite. Ilmenite taken from these rock deposits and also some sand deposits frequently contains 35 to 55 percent TiO_2.[2] In upgrading ilmenite ores from sands, approximately 2 percent of the feed from the dredge is titaniferous material, of which approximately 70 percent is recovered in the final product.[1] Table 5 gives the quantities of reagents used in the flotation process.[4]

Table 5. REAGENT USE IN FLOTATION CIRCUIT OF MILL AT OPEN-PIT MINE

Reagent	Purpose	Consumption, kg/metric ton of ore milled
Tall oil	Frother	1.33
Fuel oil	Frother	0.90
Methyl amyl alcohol	Frother	0.008
Sodium bifluoride	Depressant	0.76
Sulfuric acid	pH Modifier	1.775

3. Operating Parameters - Except in the drying step, where the temperature is maintained at 110°C, the process is carried out at ambient conditions.

4. Utilities - Electric power is required for operation of screen mills, dry mills, pumps, and other equipment. Oil or gas fuel is required for the drying step.

5. Waste streams - The large quantities of ilmenite sands handled in the upgrading operations present significant waste disposal problems. Essentially all of the waste material is returned to the vicinity of its original location. These tailings constitute a considerable solids burden on the body of water in which the material is being mined. Environmental restrictions may also preclude expansion of mine production.[2] Table 6 gives chemical composition of raw waste water from two dredge mills.[3] Atmospheric particulate emissions from separation of dredged materials are 5.0 kg/ton of product.[4]

Wet processing of the rock deposits results in a large quantity of sludge in which ilmenite is recovered by flotation.[1] Table 7 gives the chemical composition of waste water discharges and recycled water at the only operating open-pit mine.[3] The waste water from this mine is discharged

Table 6. CHEMICAL COMPOSITION OF RAW WASTE WATER AT TWO DREDGE MILLS

Parameter	Raw waste water concentration, mg/l		Treated effluent concentration, mg/l	
	Mill A	Mill B	Mill A	Mill B
Conductivity	200[a]	40[a]	280[a]	255[a]
Color	51,400[b]	16,240[b]	75[b]	13[b]
Turbidity (JTU)	<0.1	0.54		
TDS	1,644	370	96	172
TSS	11,000	209	11	4
Acidity	47.2	31.4		
Alkalinity	47.6	3.4		
COD	1,338	362	14.4	12.8
TOC	972	321	6.8	3.8
Total Kjeldahl N	0.65	0.65		
Oil and grease	400	40.0	1.0	1.0
MBAS surfactants	<0.01	<0.01		
Al	69.0	15.0		1.0
As	0.05	0.03	0.01	0.01
Be	<0.002	<0.002		
Ba	<0.5	<0.5		
B	0.10	0.04		
Cd	<0.002	<0.002		
Ca	0.10	<0.05		
Cr	0.03	<0.01	<0.01	<0.01
Cu	<0.03	<0.03	<0.03	<0.03
Total Fe	4.9	0.93	0.25	0.12
Pb	<0.05	<0.05		
Mg	1.63	0.66		
Total Mn	0.036	0.01	<0.01	0.04
Ni	<0.01	<0.01		
Tl	<0.1	<0.1		

Table 6 (continued). CHEMICAL COMPOSITION OF RAW WASTE WATER AT TWO DREDGE MILLS

Parameter	Raw waste water concentration, mg/l		Treated effluent concentration, mg/l	
	Mill A	Mill B	Mill A	Mill B
V	<0.5	<0.5		
K	3.5	1.3		
Se	<0.05	<0.05		
Ag	<0.01	<0.01		
Na	27.0	5.0		
Sr	<0.05	<0.05		
Te	<0.06	<0.15		
Ti	<0.2	0.40	<0.2	<0.2
Zn	0.014	0.002		<0.002
Mo	<0.1	<0.1		
Co	<0.1	<0.1		
Chloride	30.0	15.0		
Fluoride	0.03	<0.01		
Phosphate	0.35	0.40		
Phenol	<0.01	<0.01		

[a] Value in micromhos/cm.

[b] Value in color units.

Table 7. CHEMICAL COMPOSITIONS OF RAW WASTE WATER AND TREATED RECYCLE WATER FROM THE MILL AT OPEN-PIT MINE

Parameter	Raw waste water concentration, mg/l	Treated recycle water concentration, mg/l
Conductivity	650[a]	490[a]
Color	18.0[b]	
Turbidity (JTU)	2.2	0.56
TDS	518	526
TSS	26,300	2
Acidity	6.0	
Alkalinity	81.4	
Hardness	344.8	
COD	<1.6	
TOC	9.0	12.5
Oil and Grease	2.0	2.0
MBAS Surfac-tants	0.04	
Total Kjeldahl N	0.65	
Al	210	
As	<0.01	0.01
Be	<0.002	<0.002
B	<0.01	
Cd	<0.002	
Ca	350	
Cr	0.58	0.02
Cu	0.43	<0.03
Total Fe	500	<0.02
Pb	0.05	<0.05
Mg	187.5	
Total Mn	5.9	0.3
Ni	1.19	<0.01
Tl	<0.1	
V	2.0	<0.5
K	23.7	
Se	0.132	
Ag	0.015	
Na	41	

Table 7.(continued). CHEMICAL COMPOSITIONS OF RAW WASTE WATER AND TREATED RECYCLE WATER FROM THE MILL AT OPEN-PIT MINE

Parameter	Raw waste water concentration, mg/l	Treated recycle water concentration, mg/l
Sr	0.29	
Te	<0.06	
Ti	2.08	<0.2
Zn	7.6	<0.002
Mo	<0.1	
Co	<0.1	
Phenol	<0.01	
Chloride	19.1	
Fluoride	32.5	
Sulfate	213	
Nitrate	0.68	0.50
Phosphate	<0.05	
Hg	0.004	<0.0002

[a]Value in micromhos/cm
[b]Value in color units

to an inoperative open-pit quarry, from which the clarified water is recycled into the mill circuit.

Atmospheric particulate emissions from separation operations with ilmenite from rock deposits are 19 kg/ton of product.[4]

6. EPA Source Classification Code - None exists.

7. References:

1. Miller, A. Titanium, A Materials Survey. Bureau of Mines Information Circular 7791. United States Department of Interior, Washington, D. C., U.S. Govenment Printing Office, September 1957.

2. Stamper, J. W. Titanium. In: Mineral Facts and Problems, U.S. Department of Interior. Washington, D. C., U.S. Government Printing Office, 1970.

3. Calspan Corporation. Development Document for Effluent Limitations Guidelines and Standards of Performance for the Ore Mining and Dressing Industry Point Source Category (Draft). EPA Contract No. 68-01-2682. April 1975.

4. GCA Corporation. National Emissions Inventory of Sources and Emissions of Titanium. EPA Publication No. 450/3-74-008. Distributed by National Technical Information Service. May 1973.

TITANIUM METAL PRODUCTION PROCESS NO. 3

Smelting

1. Function - Smelting is done to upgrade certain ores containing large quantities of iron. The ore is crushed with coal and smelted with suitable fluxes in an electric furnace to produce iron and a slag. The titanium-rich slag is recovered from the process. This process is used only in Canada; there are no reports of commercial production of slag in the United States.[1]

2. Input Materials - The main raw material for smelting is low-grade ferruginous ilmenite (35 percent TiO_2). The process yields pig iron and a rich titanium slag of 70 percent TiO_2.[2]

3. Operating Parameters - Not available.

4. Utilities - Heat for melting is provided by electric energy to the furnace.

5. Waste Streams - Environmental problems resulting from this process probably are typical of those involved in the smelting aspects of the iron-making industry. Technology is available for the control of fumes from such processes. Slag quenching may result in emissions of hydrogen sulfide and other undesirable volatiles. Water pollution from quenching may also be significant. Ultimate disposal of the processed slag constitutes a solid wastes problem.

6. EPA Source Classification Code - None exists.

7. References:

1. Stamper, J. W. Titanium. In: Minerals Yearbook. U.S. Department of Interior. Washington, D. C., U.S. Government Printing Office, 1970.

2. Kirk-Othmer. Titanium and Titanium Alloys. In: Encyclopedia of Chemical Technology. New York, John Wiley and Sons, Inc., 1968.

TITANIUM METAL PRODUCTION PROCESS NO. 4

Chlorination and Purification

1. Function - Titanium tetrachloride is produced by the direct chlorination of a titanium dioxide concentrate consisting of rutile, ilmenite, or slag. Ilmenite ores cannot be chlorinated economically because large quantities of chlorine are consumed by its iron content. Ilmenite therefore is chlorinated only after removing its iron content by smelting. The ores (rutile is preferred) are chlorinated in batch furnaces, in fluidized beds, or in molten salt. The charge consists of the TiO_2 concentrate, about 20 to 25 percent petroleum coke, and chlorine gas. The fluidized-bed method lends itself to continuous operation. The $TiCl_4$ is purified to a clear, colorless liquid by filtration followed by fractional distillation or rectification. Stoichiometric amounts of water are added to precipitate the aluminum as aluminum oxychloride. The filtration removes solid impurities present such as sodium, calcium and magnesium compounds. Vanadium can be removed by distillation or alternatively as a sulfide by addition of H_2S.[1]

2. Input Materials - The process requires about 1.1 to 1.2 kilograms of rutile, 0.15 kilogram of chlorine and 0.15 kilogram of petroleum coke to produce enough titanium chloride to make 1 kilogram of titanium sponge.[2] Table A-2 in appendix A gives the range of composition of titanium concentrates.

3. Operating Parameters - Chlorination takes place in the temperature range of 800 to 1000°C and at atmospheric pressure.[1]

4. Utilities - The furnace is heated by electricity or by burning fuel. Since the reaction is slightly exothermic, little or no additional energy is required once the operating temperature is achieved.

5. Waste Streams - Effluent gases resulting from the manufacture of $TiCl_4$ have been reported to include 38 kilograms of Cl_2, 13 kilograms of HCl, and 12 kilograms of $TiCl_4$ per ton of $TiCl_4$ produced. Carbon dioxide and monoxide are also present in the exit gases. These emis-

sions are controlled by water scrubbers and occassionally caustic scrubbers. If the scrubber effluent becomes acidified, chlorine may be released into the atmosphere. Waste metal chlorides can release HCl if they are exposed to moisture in the atmosphere. These wastes are usually quenched and hydrolyzed, and injected into deep wells or disposed of in impounding ponds.[3] Any leakage or spill of $TiCl_4$ from product handling causes $TiCl_4$ to react strongly with water including the water vapor in the air to produce titanic and hydrochloric acids.

Increasing regulation of ocean dumping and land disposal operations is of concern to processers. The chloride disposal problem is generally considered much less severe than the problem of disposal of sulfates and acids from other processes. Technologies that will eliminate formation of chloride wastes are being sought.

6. EPA Source Classification Codes - Chlorination - 3-03-012-01.

7. References:

1. Kirk-Othmer. Titanium and Titanium Alloys. In: Encyclopedia of Chemical Technology. New York, John Wiley and Sons, Inc., 1968.

2. Stamper, J. W. Titanium. In: Mineral Facts and Problems. U.S. Department of Interior, Washington, D.C., U.S. Government Printing Office, 1970.

3. Control Techniques for Chlorine and Hydrogen Chloride Emissions. (Unpublished draft copy). Environmental Protection Agency. March 1971.

4. Baroch, C.T. et al. Titanium Plant at Boulder City, Nev.: Its Design and Operation. Bureau of Mines Report of Investigation 5141. United States Department of Interior, Washington, D.C., U.S. Government Printings Office, September 1955.

TITANIUM METAL PRODUCTION PROCESS NO. 5

Reduction

1. Function - Nearly all the current production of titanium metal involves reduction of titanium tetrachloride with magnesium in a closed system by the Kroll process. Sometimes sodium is the reductant instead of magnesium. In the magnesium process, cleaned magnesium ingots are first placed in the bottom of the reactor (a steel pot). The reactor is then sealed, evacuated, back-filled with argon, and preheated to about 700°C. Purified $TiCl_4$ is admitted at a controlled rate to maintain the temperature between 850 and 900°C. Spongy magnesium metal and liquid magnesium chloride are formed. The magnesium chloride is drained and recycled through electrolytic cells to recover the magnesium and chlorine. After the addition of titanium tetrachloride is stopped, the reactor is heated to about 900°C to completely reduce all the $TiCl_4$. When the reactor has cooled, the spongy mass is removed. After crushing the sponge, excess magnesium chloride or sodium chloride can be removed by vacuum distillation at temperatures up to 925°C or by leaching in dilute hydrochloric acid and drying.[1] Vacuum distillation has advantages over the leaching process which introduces oxygen, nitrogen and hydrogen into the sponge titanium.[2]

2. Input materials - Production of 1 kilogram of titanium sponge metal requires approximately 2.5 kilograms of rutile, 5 kilograms of chlorine, 1.25 kilograms of magnesium, 56 liters of inert gas, and about 0.3 kilogram of petroleum coke.[3] Approximately 4 kilograms of magnesium chloride are produced for each kilogram of titanium.[4] If the magnesium chloride is processed to recover its elemental constituents, producing 1 kilogram of sponge metal requires only about 0.2 kilogram of magnesium and 1 kilogram of chlorine.[3] The common dissolved impurities in titanium tetrachloride raw material are chlorine, carbonyl chloride or phosgene, carbonyl sulfide, and hydrochloric acid in gaseous form; various chlorides such as carbon tetrachloride, carbon disulfide, and several sulfur

chlorides in liquid form; and many metal chlorides of which those of silicon, vanadium, and iron are almost always present.[1]

3. Operating Parameters - Reduction takes place at temperatures from 850 to 900°C. The excess salt is removed at a temperature of 925°C by vacuum distillation.[1] The distillation is carried out at a final vacuum below 100 microns absolute pressure for 31 hours to bring both the magnesium and chloride content of the sponge below 0.1 percent.[5]

4. Utilities - Power requirements range from 13 to 33 kilowatt-hours per kilogram of sponge. The higher demand includes power to recover reductant metal and chlorine.[3] The vessel is cooled by water circulation.

5. Waste stream - Vent streams from the reactor vessel contain $TiCl_4$ and $MgCl_2$ vapors, reduced titanium chlorides, and inert argon or helium. These waste streams must be controlled by scrubbers to prevent $TiCl_4$ from reacting with moisture in the atmosphere to produce titanium hydrate fumes and HCl.[4] Conventional waste disposal techniques are employed to handle impurities in the sponge that are stripped out by distillation. Although some of the material may be drummed and sold to refiners of other materials, most of the waste, mainly in the form of metallic chlorides, is deposited in landfills or dumped at sea. Landfill material is a potential groundwater pollutant.[6]

6. EPA Source Classification Code - None exists.

7. References:

1. Kirk-Othmer. Titanium and Titanium Alloys. In: Encyclopedia of Chemical Technology. New York, John Wiley and Sons, Inc., 1968.

2. Baroch, C.T. et al. Titanium Plant at Boulder City, Nev.: Its Design and Operation. Bureau of Mines Report of Investigation 5141. United States Department of Interior, Washington, D.C., U.S. Government Printing Office, September 1955.

3. Stamper, J. W. Titanium In: Mineral Facts and Problems, Volume I, U.S. Department of Interior. Washington, D. C., U.S. Government Printing Office, 1970.

4. Control Techniques for Chlorine and Hydrogen Chloride Emissions Environmental Protection Agency. March 1971. (Unpublished Draft Copy).

5. Baroch, C.T., and T. B. Kaczmarek. Titanium Plant at Boulder City, Nev.: Operating Costs. Bureau of Mines Report of Investigation 5248. United States Department of Interior. Washington, D.C.,U.S. Government Printing Office, July 1956.

6. Report of Proposal for Liquid and Gaseous Waste Treatment for Integrated Titanium Facilities. Oregon Metallurgical Corporation. Albany, Oregon. August 1969.

TITANIUM METAL PRODUCTION PROCESS NO. 6

Melting and Ingot Conditioning

1. Function - The main features of this process are a cylindrical water-cooled copper crucible, a consumable electrode, and a vacuum system. The sponge and scrap to be melted, along with desired alloying elements, are pressed into a large electrode. A small amount of sponge in the bottom of the crucible acts as the other electrode. The furnace is tightly sealed to prevent contamination by air or other gases and melting is carried out under a vacuum or in an inert atmosphere of argon or helium. The ingots formed in the process are commonly remelted to improve homogeneity and to reduce the gas content of the metal.[1] Surfaces of ingots made by melting usually contain pits, cavities, and pieces of incompletely melted sponge. For this reason most producers must remove the outer surface of the ingot in a lathe prior to forging and rolling. This operation produces 5 to 10 percent scrap metal, which is remelted in subsequent batches. The ingot is conditioned by grinding off surface imperfections before it is sent to a fabrication mill.

2. Input Materials - Table 8 gives a material balance for the melting and ingot conditioning process.[2] Table A-6 in the appendices gives the composition of a typical titanium sponge.

Table 8. MATERIAL BALANCE FOR MELTING OPERATIONS AT TITANIUM PLANTS

Constituents	Quantity, tons
Input	
Sponge	0.544
Alloys	0.047
Scrap (purchased)	0.185
Melt scrap	0.059
Fabrication scrap	0.240
Output	
Conditioned ingot	1.0
Melt loss	0.0154
Melt scrap for recharging	0.059

3. Operating conditions - The melting operation is conducted under a vacuum ranging from 0.05 to 0.5 mm Hg for both commercially pure and alloy grades; an exception is processing of the higher-manganese alloys, in which a lower vacuum of 10 to 15 mm Hg is maintained.[3] In the processing, the crucible mix is heated to about 1800°C.[4]

4. Utilities - Typical melting currents run between 1250 and 2550 amperes at 40 to 60 volts DC.[5] Total electricity requirements for melting and conditioning are estimated to be 5.0 kilowatt-hours per kilogram of ingot.[2]

5. Waste Streams - One source reports that there are no emissions from this process.[5] About 6 percent of melt scrap from the process is recovered and recharged. About 1.5 to 2 percent of the melt is lost from the operation.

6. EPA Source Classification Code - None exists.

7. References:

1. Kirk-Othmer. Titanium and Titanium Alloys. In: Encyclopedia of Chemical Technology, New York, John Wiley and Sons, Inc 1968.

2. Kellogg, H. H. What the Future Holds for Titanium. Engineering and Mining Journal. April 1955.

3. Whitemer, V. W. Titanium Production and Use. (Presented at American Iron and Steel Institute Annual Meeting. May 1957.)

4. Barksdale, Jelks. Titanium, Its Occurence, Chemistry, and Technology. New York, The Ronald Press Company, 1966.

5. GCA Corporation. National Emissions Inventory of Sources and Emissions of Titanium. EPA Publication No. 450/3-74-000. Distributed by National Technical Information Service. May 1973.

TITANIUM METAL PRODUCTION PROCESS NO. 7

Fabrication

1. Function - Fabrication of titanium is similar to that of stainless steel. A great variety of shapes are produced including bars, billets, sheets, tubes and light plates. In the mill products, the pickup of oxygen and nitrogen is generally limited to the surface. In bars, billets, or forgings, this surface is removed by final turning, machining, or other finishing operations. In sheets or strip products, the contaminants are eliminated by grinding a few thousandths of a centimeter from the surface in the finishing operation.

2. Input Materials - Table 9 shows a material balance for the fabrication of mill products.[1]

Table 9. MATERIALS BALANCE FOR FABRICATION OF MILL PRODUCTS

Material	Quantity, tons
Conditioned ingots to be fabricated	1.434
Mill products	1.0
Fabrication scrap produced (charged to melting unit)	0.344
Fabrication loss	0.09

A commercially pure grade of titanium referred to as RS-40 is a high-purity titanium having moderate strength, good ductility, and excellent formability. An intermediate-strength grade, RS-55, has good formability. One of the highest-strength grades of commercially pure titanium is RS-70. All of these products are available in the form of sheets, plates, strips, billets, bars, wire, and welded tubing.[2]

3. Operating Parameters - Forming is done in the temperature range of 200 to 320°C.

4. Utilities - Electric furnaces are usually used for the heating. Gas-fired furnaces are also used, but to maintain uniformity of temperature, the flame must not touch the metal.[3] Data on quantities of electricity and fuel used are not available.

5. Waste Streams - metal finishing operations are a source of waste streams.

6. EPA Source Classification Code - None exists.

7. References:

1. Kellogg, H. H. What the Future Holds for Titanium. Engineering and Mining Journal. April 1955.

2. Whitmer, V. W. Titanium Production and Use. (Presented at American Iron and Steel Institute Annual Meeting. May 1957.)

3. Kirk-Othmer. Titanium and Titanium Alloys. In: Encyclopedia of Chemical Technology, New York, Wiley and Sons, Inc., 1968.

TITANIUM DIOXIDE PRODUCTION

The major segment of this industry is the manufacture of titanium dioxide (TiO_2). This compound is produced either by the chloride or the sulfate process as shown in Figure 2. In the chloride process the purified titanium dioxide is calcined or more commonly wet finished to remove residual chlorine or any hydrochloric acid that may be formed in the reaction. In the sulfate process the ore or slag is dissolved in sulfuric acid. The titanium in the solution is precipitated by hydrolysis and is calcined to produce titanium dioxide.

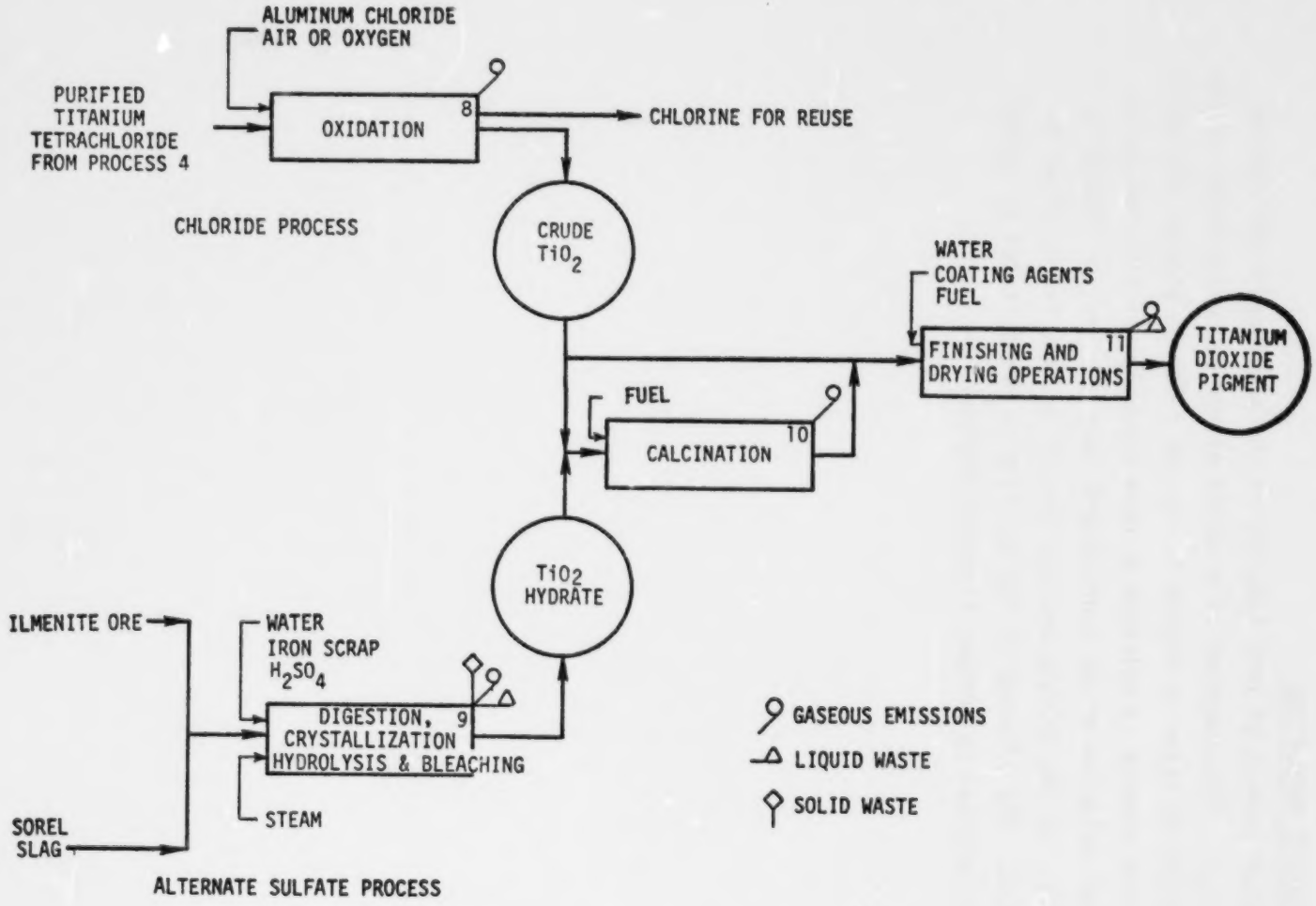

Figure 2. Titanium dioxide production.

TITANIUM DIOXIDE PRODUCTION PROCESS NO. 8

Oxidation

1. Function - Purified titanium tetrachloride vapor is fed to a reaction chamber with air or oxygen, where combustion occurs. The titanium dioxide forms as a fine smoke, which is collected by fabric filters. The liberated chlorine is also collected separately and reused. The recovered titanium dioxide, which contains some residual chlorine or any HCl formed in the reaction, may be calcined. Aluminum chloride is added to the titanium chloride to ensure complete oxidation of the titanium.

In alternate methods, the $TiCl_4$ can be reacted with water vapor to produce titanium dioxide and hydrochloric acid, or hydrolized to produce titanic acid (H_2TiO_3) and HCl. The titanic acid must then be precipitated and ignited to produce titanium dioxide.[1]

2. Input Materials - To produce one ton of titanium dioxide about 0.4 to 0.5 ton of oxygen, 1.1 to 1.2 tons of rutile and 0.03 ton of aluminum chloride are required.[2]

3. Operating Parameters - The reaction is exothermic and can be carried out continuously at about 1000°C. No reaction occurs below 600°C.[1]

4. Utilities - Additional heat is supplied externally by burning gas or oil because the heat evolved by the reaction is not sufficient to maintain the reaction.

5. Waste Streams - There are no significant wastes from oxidation.[3]

6. EPA Source Classification Code - None exists.

7. References:

1. Kirk-Othmer. Titanium and Titanium Alloys. In: Encyclopedia of Chemical Technology, New York, Hohn Wiley and Sons, Inc., 1968.
2. Stamper, J. W. Titanium. In: Mineral Facts and Problems, Volume I, U. S. Department of Interior. Washington, D. C., U.S. Government Printing Office, 1970.
3. Private communication, J. L. Jones, Stanford Research Institute to Research Triangle Institute. July 15, 1976.

TITANIUM DIOXIDE PRODUCTION PROCESS NO. 9

Digestion, Crystallization, Hydrolysis, and Bleaching

1. Function - In the sulfate process, ilmenite ore or Sorel slag are digested in sulfuric acid with steam added for heating the solution. Scrap iron is added as a reducing agent to convert all of the ferric iron to ferrous iron (0.5 kg Fe/kg Fe_2O_3 in ore). Sorel slag has essentially no Fe_2O_3 present and thus requires no scrap iron addition while an Australian ilmenite contains in excess of 15 weight percent of Fe_2O_3 and may require up to 0.16 kilogram of scrap iron/kilogram of TiO_2 product. When an ilminite ore is used, up to 75 percent of the ferrous iron is removed from the digestion liquor by crystallization. Because of the much lower iron content of the Sorel slag and no need to add scrap iron, the iron content does not have to be reduced before hydrolysis.

In the hydrolysis reactor, a hydrous titanium oxide is produced and filtered with an 18 percent H_2SO_4 filtrate solution produced which is only partially recycled with the majority (1.5 H_2SO_4 kg/kg TiO_2) sent to waste disposal. This stream is typically referred to as the strong acid waste. Washing of the hydrolysis cake plus an acid leaching operation (called bleaching) that follows filtration, produces about 0.9 kilogram H_2SO_4. This stream is called the weak acid waste. The total quantity of waste acid produced does not vary greatly for plants using ilmenite ores or Sorel slag.

The hydrous oxide product after bleaching (for removal of remaining trace impurities such as iron or chrome) is sent to a calciner. The TiO_2 product from calcining is usually subjected to a wet finishing (and coating) operating and dried although some material is shipped uncoated.

2. Input Materials - The quantities of raw materials used vary considerably depending on the grade and source of the titanium raw material. Table 10 gives the estimated requirements of raw materials for producing titanium dioxide.[2]

Table 10. MATERIALS REQUIRED FOR PRODUCING ONE TON OF TITANIUM DIOXIDE

Material	Quantity, tons
Ilmenite	1.9-2.6
Sorel Slag	~1.6
Sulfuric acid (60° Baume)	
Ilmenite Ore	3.75-4.5
Sorel Slag	~2.7
Iron scrap (Ilmenite ore only)	0.15-0.2

3. Operating Parameters - During the exothermic reaction, the reaction temperature rises rapidly from 125 to 200°C.[1]

4. Utilities - Steam and electric power are used.

5. Waste Streams - This process produces four times as much waste as the chloride process. The waste stream contains 2.4 kilograms of sulfuric acid, 1.5 kilograms of ferrous sulfate, 0.15 kilogram of other sulfates, and 0.06 kilogram of other metal salts including variable but small amounts of vanadium and chrominum for each kilogram of titanium dioxide produced.[3] Of the total waste sulfuric acid, approximately 90 percent consists of weak (1.35%) acid with the balance consisting of 18 percent acid. The leachates and dilute acid resulting from the hydrolysis are the principal waste products of this operation. Until recently one producer discharged acid and sulfate wastes in the ocean. Acid wastes are neutralized and diluted before being discharged.

Particulate air pollutants from titanium dioxide production are usually controlled by wet scrubbing. A cyclone or electrostatic precipitator may precede the scrubber.

When ilmenite ore is used 2 to 4 kilograms of coppers ($FeSO_4 \cdot 7H_2O$) are produced per kilogram of TiO_2.

6. EPA Source Classification Code - None exists.

7. References:

1. Kirk-Othmer. Titanium and Titanium Alloys. In: Encyclopedia of Chemcial Technology, New York, John Wiley and Sons, Inc., 1968.

2. Stamper, J. W. Titanium. In: Minerals Facts and Problems. United States Department of Interior. Washington, D. C., U.S. Government Printing Office, 1970.

3. Heavy Going Ahead for Waste Discharging at Sea. Chemical Week. June 27, 1973.

TITANIUM DIOXIDE PRODUCTION PROCESS NO. 10

Calcination

1. Function - The titanium dioxide hydrate from the digester is calcined in direct-fired, inclined rotary kilns. As the charge travels through the kiln, it is first dried, then water and SO_3 are driven off. The kiln temperature is carefully controlled according to the grade of pigment being made.

The titanium dioxide resulting from the chloride process may occassionally be calcined to remove residual chlorine and any hydrochloric acid that is formed in the reaction. This is not common practice.

2. Input Materials - Titanium dioxide.

3. Operating Parameters - The kiln temperature may reach 1000°C in the sulfate process.[1] In calcination of the titanium dioxide resulting from oxidation in the chloride process, the temperature is maintained at about 500 to 600°C.[2]

4. Utilities - Oil or gas is used as fuel. Data on quantities of fuel requirements are not available. Electric power is also used.

5. Waste Streams - Emissions from the sulfate process calciner contain sulfur dioxide, sulfur trioxide, sulfuric acid mist, and particulate matter. Limited field test data indicate that 20 kilograms of SO_2 are emitted per ton of calcined titanium oxide.[3] The gases leave the calciner at temperatures of 370 to 480°C and at a rate of 45 m^3 per kilogram of product. Sulfur emissions result from sulfuric acid carryover in the digested product. Emissions are controlled by scrubbers and electrostatic precipitators. Atmospheric emissions from one calcining operation were reported to be: 1320 kg of SO_2/day, 70 kg of SO_3/day, 172 kg of particulate/day and 82 kg of acid mist/day. No process through-put data were provided. Table 11 gives typical composition of calciner exhaust gases before treatment.[4]

Table 11. ANALYSIS OF EFFLUENT GASES OF A TiO_2 CALCINER[a]

Materials	Percent by volume
N_2	54.0
H_2O	35.0
O_2	7.0
CO_2	4.0
$SO_3 + SO_2$	0.3
$TiO_2(gm/m^3)$	2.3

[a] Calculated from material balance

6. EPA Source Classification Code - None

7. Reference:

1. Kirk-Othmer. Titanium Compounds. In: Encyclopedia of Chemical Technology, New York, John Wiley and Sons, Inc., 1968.

2. Report of Atmospheric Emissions Tests Conducted at Titanium Division, National Lead Company, Sayerville, New Jersey. U.S. Department of Health, Education and Welfare. 1967.

3. U. S. Environmental Protection Agency. Miscellaneous Sources. In: Control Techniques for Sulfur Oxide Air Pollutants. (Advisory Committee Draft). Nov. 20, 1972.

4. Sittig, M. Titanium. In: Pollutant Removal Handbook. New Jersey, Noyes Data Corp., 1973.

TITANIUM DIOXIDE PRODUCTION PROCESS NO. 11

Finishing Operations

1. Function - Some pigment is sold for general purposes in the form in which it leaves the calciner. The remainder usually requires wet milling to remove oversized particles and to break up aggregates. Surface coating is applied to a major portion of the pigment produced in order to increase resistance to chalking, discoloration and fading. The final product is then dried in a dryer.
2. Input Materials - Most of the titanium dioxide from calcination requires milling. Surface coatings include such agents as hydrous alumina, chromic oxide, silica and zirconium compounds.[1] Alternatively small proportions of conditioning agents such as antimony trioxide or zinc oxide may be added before calcination.
3. Operating Parameters - Milling is done at ambient conditions.
4. Utilities - Energy is needed by milling equipment.
5. Waste Streams - TiO_2 dust emissions are generally well controlled. Waste water from the milling operation amounts to 46 liters per kilogram of TiO_2. This water may contain ammonium or sodium sulfate.
6. EPA Source Classification Code - None exists.
7. Reference

1. Barksdale, Jelks. Titanium, Its Occurrence, Chemistry and Technology. New York, The Ronald Press Company, 1966.

APPENDIX A

COMPOSITION AND PROPERTIES OF TITANIUM PRODUCTS

Table A-1. ANALYSIS OF ILMENITE ORE[1]

(percent)

Chemical constituent	Piney River	Roseland	New York	Florida	California
TiO_2	44.3	51.4	44.4	64.1	48.2
FeO	35.9	37.9	36.7	4.7	39.1
Fe_2O_3	13.8	1.6	4.4	25.6	10.4
SiO_2	2.0	4.6	3.2	6.3	1.4
Al_2O_3	1.21	0.55	0.19	1.5	0.2
P_2O_3	1.01	0.17	0.07	0.21	
ZrO_2	0.55		0.06		0.05
MgO	0.07	2.35	0.80	0.35	0.6
MnO	0.52	0.70	0.35	1.35	0.1
CaO	0.15	0.59	4.0	0.13	0.1
V_2O_5	0.16	0.07	0.24	0.13	0.05
Cr_2O_3	0.27		0.001	0.1	0.03
SnO_2	0.001	0.02	0.001		0.001
CuO	0.0005	0.0005	0.004		0.005
CoO	0.005				
PbO	0.005				
NiO	0.05				
WO_3					0.005

Table A-2. RANGE OF COMPOSITION OF TITANIUM CONCENTRATES[2]

	Ilmenite	Rutile	Titanium slag from Canada
Titania (TiO_2)	37 to 65	94 to 98	71.4
Iron oxide (Fe_2O_3)	30 to 55	0.2 to 1.5	16.3
Silica (SiO_2)	0.5 to 3.0	0.2 to 2.0	3.8
Alumina (Al_2O_3)	0.2 to 1.5	0.2 to 0.5	4.6
Calcium (CaO)	0.1 to 1.0	0.02 to 0.08	0.8
Magnesium (MgO)	0.05 to 4.0	0.02 to 0.09	5.0
Chromium (Cr_2O_3)	0.01 to 0.5	0.1 to 0.3	0.2
Vanadium (V_2O_5)	0.05 to 0.5	0.4 to 0.8	0.6
Zirconium (ZrO_2)	0.4 to 2.0	0.01 to 0.4	-

Table A-3. CHEMICAL ANALYSIS OF TITANIUM METAL[3]

Constituent	Grade 40	Grade 55	Grade 70
Carbon	0.05	0.05	0.05
Nitrogen	0.01	0.012	0.015
Iron	0.15	0.20	0.20
Titanium	Balance	Balance	Balance
Hydrogen			
in bar & billet	0.0125 max	0.0125 max	0.0125 max
in sheet & strip	0.0150	0.0150	0.0150
Density	2.61 kg /m^3		

Table A-4. PHYSICAL PROPERTIES OF COMMERCIALLY PURE TITANIUM[4]

Atomic number	22
Atomic weight	47.90
Density, g/ml	4.507
Melting point, °C	1668
Boiling point, °C	3535
Allotropic transformation temperature, °C	822
Heat of fusion, cal/mole	5000
Heat of sublimation at 25°C, cal/mole	111,720
Specific heat, 0-500°C, cal/(g)(°C)	0.1386
Entropy, 25°C, cal/(mole)(°C)	7.24
Thermal expansion coefficient at 25°C, per °C	8.5×10^{-6}
Thermal conductivity, 25°C, cal/(sec)(cm^2)(°C/cm)	9.41
Emissivity	9.43
Electrical resistivity, 25°C, μΩ-cm	47.8
Magnetic susceptibility, cmu/g	3.17
Modulus of elasticity, psi x 10^6	
tension	~14.7
compression	15.0
shear	6.4
Poisson's ratio	~0.41

Table A-5 . PHYSICAL PROPERTIES OF TITANIUM DIOXIDE[5]

	TiO_2
Melting point	1640°C
Boiling point	2700°C
Density	4.2 g/cc
Atomic weight	79.9

Table A-6. TYPICAL TITANIUM SPONGE ANALYSIS[4]

Element, %, max.	Percent by wt, dry[a]			
	Grade[b] 1A-0			Grade[b] 1B-0
	A	B	C	A
Nitrogen	0.015	0.015	0.010	0.015
Carbon	0.020	0.025	0.020	0.020
Sodium (total)			0.19	
Magnesium	0.08	0.40		0.08
Chlorine	0.12	0.15	0.20	0.12
Iron	0.12	0.10	0.05	0.05
Silicon	0.04	0.04	0.04	0.04
Hydrogen	0.005	0.03	0.05	0.005
Oxygen	0.10	0.10	0.10	0.07
Water	0.02	0.02	0.02	0.02
All other impurities (total)	0.05	0.05	0.05	0.05
Titanium balance (nominally)	99.3	99.1	99.3	99.3

[a]Dried

[b]Grades consist of the following types: A, magnesium-reduced and vacuum-distilled; B, magnesium-reduced and acid-leached; C, sodium-reduced and acid-leached.

Table A-7. CHEMICAL ANALYSES OF COMMERCIAL GRADE AND PURIFIED $TiCl_4$ FROM SOURCES A AND B [6]

(Grams/liter)

Source	Fe	V	S	Si	Free Cl_2	Nonvolatile residue	Spectrographic trace elements
A	0.03	1.9	0.15	0.26	2.00	1.7	Cu,Al,Pb,Mg,Mn,Ca,Cr,Sn
A	0.04	1.9	0.04	0.40	1.90	1.75	Cu,Al,Pb,Mg,Mn,Ca,Cr
A	0.03	1.7	0.03	0.25	1.98	3.4	Cu,Al,Pb,Mg,Mn,Ca,Ni
A	0.04	1.2	0.05	0.25	1.02	5.4	Cu,Al,Pb,Mg,Mn,Ca,Cr
A	0.04	1.1	0.03	0.25	1.30	5.9	Cu,Al,Mg,Mn,Ca
B	0.05	1.8	0.06	0.27	2.97	1.70	Cu,Al,Mg,Mn,Ca,Fe,Sn,Nb
B	0.04	1.9	0.04	0.40	1.90	1.76	Cu,Al,Mg,Mn,Ca,Fe,Pb,Cr
B	0.03	1.7	0.03	0.25	1.98	3.40	Cu,Al,Mg,Mn,Ca,Fe,Pb,Ni
B	0.04	1.1	0.03	0.25	1.30	5.90	Cu,Al,Mg,Mn,Ca,Fe
B	0.03	0.95	0.04	0.15	3.55	4.20	Cu,Fe,Sn,Mo
Range of typical)	0.03		0.01		<0.10		
purified $TiCl_4$)	0.04	<0.10	0.08	<0.10	0.15		

Table A-8. PHYSICAL PROPERTIES OF TITANIUM TETRACHLORIDE[7]

Color	None
Density, 20°C, g/ml	1.70
Freezing point, °C	-24
Heat of fusion, kcal/mole	2.249
Boiling point, °C	135.8
Vapor pressure[a] in mm Hg	
At 20°C	10.0
At 50°C	41.4
At 100°C	266
Heat of vaporization, kcal/mole	
25°C	9.1
135.8°C	8.4
Specific heat, 20°C, cal/g	0.193
Critical temperature, °C	358
Heat of formation of liquid, 25°C, kcal/mole	-192.3 ± 0.9
Viscosity, (dyn)(sec)/cm	0.0079
Refractive index, n_D^{20},	1.6085
Magnetic susceptibility	-0.287×10^{-6}
Dielectric constant, 20°C	2.79

[a] $\log_{10} P_{mm} = 7.64433 - 1947.6/273.16 + t(°C)$.

Table A-9. TYPICAL PROPERTIES OF COMMERCIAL TITANIUM ALLOYS[4]

Property	Unalloyed	Composition, wt % (balance Ti[a])					
		5Al-2.5Sn	6Al-4V	6Al-6V-2Sn	8Al-1Mo-1V	3Al-13V-11Cr	6Al-2Cb-1Ta-1Mo
Density, lb,in.^{3}	0.163	0.162	0.160	0.162	0.158	0.175	0.162
Thermal conductivity, Btu/(hr)(ft^2)(°F/ft)	9.5	4.5	4.2	4.2	3.6	4.0	3.7
Tensile modulus, psi x 10^6	15.0	16.0	16.5	16.0	17.5	14.5	17.0
Tensile strength, psi x 10^3	75	125	170[b]	185[b]	145	190[b]	115
Tensile yield strength, psi x 10^3	60	117	155[b]	175[b]	138	180[b]	110
Elongation in tension,%	25	18	8[b]	8[b]	15	8[b]	10
Charpy impact strength ft-lb	30	18	17	15	20	8	34
Creep strength (600°F, 100 hr. 0.1%)psi x 10^3	20	68	100	70	95	140	75
Fatigue strength, psi x 10^3 for 10^7 cycles	46.0	76.0	82.0	66.0	80.0	33.0	55.0
Bend radius, r/t	2	4	4.5	4.5	4.5	3	4
Weldability	excellent	excellent	good	poor	good	good	excellent

[a]Annealed condition unless otherwise noted.

[b]Solution-treated and aged condition.

APPENDIX B

TITANIUM AND TITANIUM OXIDE PRODUCERS

Table B-1. TITANIUM INDUSTRY COMPANIES, 1972 [2,8,9]

Company and location	Operation	Capacity, tons
American Cyanamid Co.		
Pigment Division at Savannah, Ga.	TiO_2 production(s)	65,300
	TiO_2 production (c)	36,300
Combustion Engineering		
Camden, N.J.	TiO_2 production	N.A.
Wilmington, De.	TiO_2 production	N.A.
Crucible Steel Co., of America		
Midland, Pa.	Ti ingot from sponge and scrap	N.A.
E.I. duPont de Nemours & Co., Inc.		
Starke, Fla.	Sand mining	
Highland, Fla.	Sand mining	
Antioch, Cal.	TiO_2 production (c)	24,500
Edgemoor, Del.	TiO_2 production (c)	101,400
New Johnsonville, Tenn.	TiO_2 production (c)	206,800
Gulf and Western Ind.		
(The New Jersey Zinc Co. Subsid)		
Ashtabula, Ohio[a]	TiO_2 production (c)	25,000
Gloucester City, N.J.	TiO_2 production (s)	39,000
Harvey Aluminum, Inc.		
Torrance, Cal.	Ti ingot from sponge and scrap	N.A.
Howmet Corp.		
Whitehall, Mich.	Ti ingot from sponge and scrap	N.A.
Humphreys Mining Co.		
Folkston, Ga.	Sand mining	

Table B-1 (Continued). TITANIUM INDUSTRY COMPANIES, 1972 [2,8,9]

Company and location	Operation	Capacity, tons
Kerr-McGee Corp.		
Hamilton, Miss.	TiO_2 production (c)	41,700
Lonza, Inc.		
Mapleton, Ill.	TiO_2 production	N.A.
NL Industries Inc.		
Tahawus, N.Y.	Rock mining	
Titanium Pigment - Divisions at St. Louis Mo.	TiO_2 production (s)	104,000
Sayreville, N.J.	TiO_2 production (s)	112,500
Oregon Metallurgical Corp.		
(Owned by Armco Steel Corp. and Ladish Co.) Albany, Oregon	Ti sponge production	N.A.
	Ti ingot from sponge production	N.A.
RMI Company		
(Owned by National Distillers and Chemical Corp. and U.S. Steel Corp.) Niles, Ohio	Ti ingot from sponge and scrap	N.A.
Ashtabula, Ohio	Ti sponge production	N.A.
SCM Corporation Glidden-Durkee Corp. Division		
Lakehurst, N.J.	Sand mining	
Baltimore, Md.	TiO_2 production (c)	22,700
	TiO_2 production (s)	48,100
Ashtabula, Ohio	TiO_2 production	25,000

Table B-1 (Continued). TITANIUM INDUSTRY COMPANIES, 1972 [2,8,9]

Company and location	Operation	Capacity, tons
Teledyne Titanium Inc.		
Monroe, N.C.	Ti ingots from sponge and scrap	N.A.
Titanium Enterprise[b]		
Green Cove Springs, Fla.	Sand mining	127,000
Titanium Metals Corp. of America (Owned by N.L. Industries Inc. and Allegheny Ludlum Steel Co.) Henderson, Nev.	Ti sponge production Ti ingots from sponge and scrap	N.A.
Titanium Technology Corp. Pomona, Cal.	Ti ingots from sponge and scrap	N.A.
Titanium West, Inc. Reno, Nev.	Ti ingots from sponge and scrap	N.A.
Transelco, Inc.		
Penn Yan, N.Y.	TiO_2 production	N.A.

[a]Leased from Cabot Corp.

[b]A joint venture of American Cyanamid and the Union Camp Corp.

[c]Chloride process

[s]Sulfate process

N.A. - not available

APPENDIX C

REFERENCES FOR APPENDICES

REFERENCES FOR APPENDICES

1. Barksdale, Jelks. Titanium, Its Occurence, Chemistry and Technology. New York, The Ronald Press Company, 1966.

2. Stamper, J.W. Titanium. In: Minerals Facts and Problems. Volume I, United States Department of Interior. Washington, D.C., U.S. Government Printing Office, 1970.

3. Whitmer, V.W. Titanium Production and Use. (Presented at American Iron and Steel Institute Annual Meeting. May 1957.)

4. Kirk-Othmer. Titanium and Titanium Alloys. In: Encyclopedia of Chemical Technology, New York, John Wiley and Sons, Inc., 1968.

5. GCA Corporation. National Emissions Inventory of Sources and Emissions of Titanium. EPA Publication No. 450/3-74-008. Distributed by National Technical Information Service. May 1973.

6. Baroch, C.T., et al. Titanium Plant of Boulder City, Nev.: Its Design and Operation. United States Department of Interior. Washington, D.C., Report of Investigation 5141. September 1955.

7. Kirk-Othmer. Titanium Compounds (Inorganic). In: Encyclopedia of Chemical Technology, New York, John Wiley and Sons, Inc., 1968.

8. Noe, F.E. Titanium. In: Minerals Yearbook, United States Department of Interior. Washington, D.C., U.S. Government Printing Office, 1971.

9. Stanford Research Institute. 1974 Directory of Chemical Producers, United States of America. Printed in USA.